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(54) COATING FILM RESIN COMPOSITION AND RESIN MOLDED ARTICLE WITH COATING FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an excellent anti-fogging coating film which has excellent anti-fogging performance and good adhesion between the coating film and a molded article and does not cause reduction in hardness of the coating film upon absorbing water.

SOLUTION: A coating film resin composition comprises 100 pts.wt. polymerizable monomer mixture composed of 10-80 wt.% polyethylene glycol di(meth)acrylate, 0.1-20 wt.% di(meth)acrylate, 0.1-40 wt.% hydrophilic monomer, and 0.1-50 wt.% colloidal silica whose surface has been modified with a hydrolyzate of a (meth)acrylic functional silane compound and a hydrolyzate of a hydrophilic non-(meth) acrylic functional silane compound, 0.1-10 pts.wt. nonionic surface active agent having an HLB of 6-11, 0.1-5 pts.wt. anionic surface active agent, and 0.01-10 pts.wt. polymerization initiator.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the resin mold goods with which the paint film which consists of a resin constituent for paint films and its hardened material was covered.

[0002]

[Description of the Prior Art] It excels in transparency, polycarbonate resin and acrylic resin are cheap and lightweight, and since shaping is easy, they are used in many fields, such as goggles, shielding, and a spectacle lens, as a substitute of glass. However, since the mold goods which consist of these resin are hydrophobicity, when there was a rapid change of temperature and humidity, or when it is put on the interface where temperature and humidity differ, the water which dewed will form detailed waterdrop on the surface of mold goods, and the cloudiness of mold goods will produce them by scattering about light. Therefore, when it is used for the application than to which greater importance is attached to fluoroscopy nature, such as goggles and shielding, the cloudiness of the mold goods by this dew condensation poses a big problem.

[0003] In order to solve such a problem, the water which dewed by carrying out surface treatment of the mold goods was absorbed or diffused, and examination which prevents the cloudiness by dew condensation has been performed.

[0004]

[Problem(s) to be Solved by the Invention] The technique which gives fog resistance is indicated by forming a paint film, making the water which carried out hydrophilization of the mold-goods front face, and dewed absorb, or making it spread by applying to a mold-goods front face the solution which contains a hydrophilic polymer, a surfactant, or them in JP,50-29656,A, JP,50-71770,A, JP,57-69043,A, and JP,2-16185,A, and drying. However, with these techniques, although fog resistance could be given, the paint film softened at the time of water absorption, and there was a fault that will become or the antifog effectiveness will disappear simply by wiping of a mold-goods front face that a blemish tends to enter.

[0005] On the other hand, the technique which forms the bridge formation paint film of a hydrophilic property in a mold-goods front face by the coating agent of a heat hardening mold is indicated by JP,54-78782,A, JP,56-8258,A, JP,57-72856,A, and JP,59-217783,A. However, the adhesion of fog resistance, paint film reinforcement, a paint film, and mold goods was not able to be raised with sufficient balance with these techniques. Moreover, an elevated temperature and long duration need to be heat-treated for formation of a bridge formation paint film, and there was a problem in respect of productivity and energy cost.

[0006] Moreover, although the technique which forms an antifog paint film by photo-curing is indicated by JP,6-136165,A, the thing excellent in all the adhesion of fog resistance, paint film reinforcement, a paint film, and a base material is not obtained.

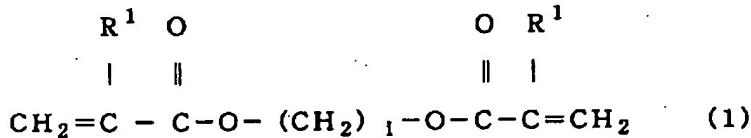
[0007]

[Means for Solving the Problem] In order to solve the above-mentioned trouble, as a result of inquiring wholeheartedly, by applying the specific resin constituent for paint films to resin mold goods, and hardening it, this invention persons were excellent in fog resistance ability, thermoforming nature, the adhesion of a paint film, and abrasion-proof nature, and found out the resin mold goods with which the outstanding paint film without the fall of the fog resistance ability by thermoforming or the degree-of-hardness fall at the time of water absorption was

covered.

[0008] That is, the summary of this invention has the following ***** polymerization nature monomer mixture 100 weight section and HLB in the resin constituent for paint films which becomes the Nonion system surfactant 0.1 of 6-11 - 10 weight sections, the anion system surfactant 0.1 - 5 weight sections list from a polymerization initiator 0.01 - 10 weight sections in the following component (a), (b), (c), and (d).

[0009] (Di(meth)acrylate b) 0.1-20 % of the weight expressed with the following general formula (1) polyethylene GURIKORUJI (meta) acrylate (a) 10 - 80% of the weight [Formula 4]



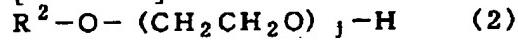
(R1 expresses H and CH₃ or i expresses the integer of 2-10.)

a component -- (a) -- and -- (b) -- copolymerization -- being possible -- a hydrophilic property -- a monomer -- (c) -- 0.1 - 40 -- % of the weight (meta) -- an acrylic -- functionality -- a silane -- a compound -- hydrolyzate -- and -- a hydrophilic property -- un-- functionality -- a silane -- a compound -- hydrolyzate -- a front face -- embellishing -- having had -- colloidal silica -- (d) -- 0.1 - 60 -- % of the weight -- the above-mentioned -- a paint film -- ** -- resin -- a constituent -- setting -- an acrylic (meta) -- functionality -- a silane -- a compound -- a sulphydryl group -- content -- a silane -- or -- the amino group -- content -- a silane -- polyethylene -- GURIKORUJI (meta) -- acrylate -- a Michael addition reaction -- an object -- from -- becoming -- things -- being desirable -- .

[0010] Moreover, it is desirable that a non-[hydrophilic] functionality silane compound consists of a Michael addition reaction object of a sulphydryl group content silane or an amino-group content silane, and a hydrophilic monofunctional (meta) acrylic monomer in the above-mentioned resin constituent for paint films.

[0011] Furthermore, in the above-mentioned resin constituent for paint films, it is desirable that the Nonion system surfactant is the compound expressed with the following general formula (2).

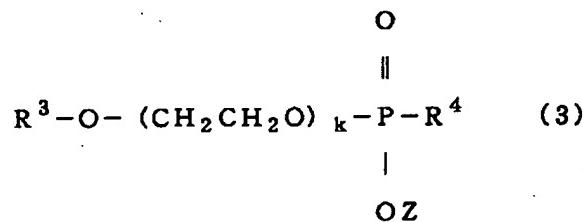
[Formula 5]



(R2 expresses an alkyl group or an alkylphenyl radical, and j expresses the integer of 1-30.)

Furthermore, in the above-mentioned resin constituent for paint films, it is desirable that an anion system surfactant is the compound expressed with the following general formula (3).

[Formula 6]



(R3 expresses an alkyl group or an alkylphenyl radical, and R4 expresses -OZ or -O-(CH₂CH₂O)_k-R3.) In Z, alkali metal or ammonium salt, and k express the integer of 1-30.

Moreover, the summary of this invention is in the resin mold goods with which the paint film which consists of a hardened material of the above-mentioned resin constituent for paint films was covered.

[0012]

[Embodiment of the Invention] As for the average molecular weight of the polyethylene GURIKORUJI (meta) acrylate (a) which is the component of the polymerization nature monomer mixture which constitutes the resin constituent for paint films of this invention, it is desirable that it is 200-2000, and it is more desirable that it is 200-1000. (Meta) Acrylate is methacrylate or acrylate. When average molecular weight is too low, the hydrophilic properties of the paint film (suitably henceforth a "paint film") which consists of a hardened material of the resin

constituent for paint films run short, and good fog resistance ability is not obtained. When too high, the degrees of hardness of a paint film run short. The adhesion (suitably henceforth "adhesion of a paint film") of a paint film and resin mold goods is good, and in order to obtain a paint film with high fog resistance ability and degree of hardness, concomitant use with a with an average molecular weight of less than 200 to 400 thing and the thing of average molecular weight 400-2000 is desirable. Concomitant use with the thing of average molecular weight 200-350 and the thing of average molecular weight 400-1000 is more desirable. The content of the polyethylene GURIKORUJI (meta) acrylate in polymerization nature monomer mixture (a) is 10 - 80 % of the weight, and it is desirable that it is 20 - 60 % of the weight.

[0013] As di(meth)acrylate (b) expressed with the general formula (1) which is the component of polymerization nature monomer mixture, 1, 4-butane JIORUJI (meta) acrylate, 1, 5-pentane JIORUJI (meta) acrylate, 1, 6-hexane JIORUJI (meta) acrylate, 1, and 9-nonane JIORUJI (meta) acrylate etc. is mentioned. The content of these di(meth) acrylate in polymerization nature monomer mixture (b) is 0.1 - 20 % of the weight, and it is desirable that it is 2 - 15 % of the weight. When a content is lower than 0.1 % of the weight and a paint film sets under high-humidity/temperature, it becomes easy to cause the degree-of-hardness fall of a paint film, and the fall of the adhesion of a paint film. Moreover, when higher than 20 % of the weight, the absorptivity of a paint film falls and good fog resistance ability is not obtained.

[0014] The hydrophilic monomers (c) which are the components of polymerization nature monomer mixture are the above-mentioned polyethylene GURIKORUJI (meta) acrylate (a) and di(meth)acrylate (b), and a hydrophilic monomer that can be copolymerized. As the concrete example, 2-hydroxyethyl (meta) acrylate, 2-hydroxy butyl (meta) acrylate, acryloyl (meta) morpholine, N, and N-dimethyl (meta) acrylamide, N, and N-dimethylaminoethyl (meta) acrylamide, N, and N-dimethylaminopropyl (meta) acrylamide, N-isopropyl (meta) acrylamide, N-vinyl pyrrolidone, polyethylene-glycol (meta) acrylate, alkyl phenoxy polyethylene-glycol (meta) acrylate, etc. are mentioned. (Meta) Acryloyl is methacryloyl one or acryloyl. (Meta) Acrylamide is methacrylamide or acrylamide. Also in these, while making good the adhesion and the hydrophilic property of a paint film, especially since the monomer of an acrylamide (meta) system can strengthen the capacity to hold a surfactant in a paint film, it is desirable. The content of the hydrophilic monomer in polymerization nature monomer mixture (c) is 0.1 - 40 % of the weight, and it is desirable that it is 1 - 20 % of the weight. When a content is lower than 0.1 % of the weight, the hydrophilic property of a paint film gets worse. When higher than 40 % of the weight, the reinforcement of a paint film, especially the paint film reinforcement at the time of water absorption fall.

[0015] The colloidal silica (d) which is the component of polymerization nature monomer mixture is colloidal silica by which the front face was embellished with the hydrolyzate of an acrylic (meta) functionality silane compound, and the hydrolyzate of a non-[hydrophilic] functionality silane compound. The content of the colloidal silica (d) with which the front face in polymerization nature monomer mixture was embellished is 0.1 - 60 % of the weight, and it is desirable that it is 20 - 60 % of the weight. It will be in the condition "the front face was embellished with hydrolyzate", and that the hydrolyzate of a silane compound was held by the condensation reaction in surface some or surface all of colloidal silica here, and will mean that reforming of the surface characteristic of colloidal silica is carried out. Moreover, the colloidal silica by which that to which the condensation reaction of hydrolyzate progressed is held at coincidence is also contained in the colloidal silica (d) "by which the front face was embellished with hydrolyzate."

[0016] This surface qualification in this invention can add a silane compound for example, to a colloidal silica sol, and can be easily performed by producing and cheating out of hydrolysis or hydrolysis, and a condensation reaction. An inorganic acid or an organic acid can be used as a catalyst at the time of performing the hydrolysis reaction of a silane compound. As an inorganic acid, halide acid, such as a hydrochloric acid, a hydrofluoric acid, and a hydrobromic acid, a sulfuric acid, a nitric acid, phosphoric acid, etc. are mentioned. As an organic acid, formic acid, an acetic acid, oxalic acid, an acrylic acid, a methacrylic acid, etc. are mentioned. As a dispersion medium of a colloidal silica sol, ether, such as ketones; tetrahydrofurans, such as alcohols; acetones, such as a water; methanol, ethanol, and isopropyl alcohol, and methyl isobutyl ketone, and dioxane, can be mentioned.

[0017] As for hydrolysis and the condensation reaction of a silane compound, it is desirable to be carried out under conditions of 30 minutes - about 24 hours at about [room temperature -120 degree C] temperature. It is more desirable to be carried out under conditions of about 1 - 10 hours at the temperature of boiling point extent of a room temperature - a solvent. Moreover (meta), when performing surface qualification of colloidal silica by the

hydrolyzate of an acrylic functionality silane compound, and the hydrolyzate of a non-[hydrophilic] functionality silane compound, after performing surface qualification by the hydrolyzate of an acrylic functionality silane compound previously (meta), it is desirable to perform surface qualification by the hydrolyzate of a non-[hydrophilic] functionality silane compound. When surface qualification is first performed by the hydrolyzate of a non-[hydrophilic] functionality silane compound, colloidal silica may condense and the good resin constituent for paint films may become hard to be obtained.

[0018] As for the hydrolyzate of the acrylic (meta) functionality silane compound which embellishes the front face of colloidal silica, it is desirable to consist of hydrolyzate of the Michael addition reaction object of a sulphydryl group content silane or an amino-group content silane, and polyethylene GURIKORUJI (meta) acrylate.

[0019] (Meta) As for the sulphydryl group content silane as a raw material of an acrylic functionality silane compound, what is expressed with the following general formula (4) is desirable.

[Formula 7]

R^5 (3-a)

|

(4)

X a S i - R⁶ - SH

(As for R5, a carbon number expresses the hydrocarbon group or fluorination alkyl group of monovalence, and R6 expresses the permutation or the unsubstituted hydrocarbon group of bivalence of 1-10.) X expresses hydrolysis nature machines, such as an alkoxy group, an amino group, and an isopropanal PENOKISHI radical, and a expresses the integer of 1-3.

As an example of R5, radicals, such as methyl, ethyl, propyl, butyl, phenyl, octadecyl, 2-phenylethyl, vinyl, 3 and 3, 3-trifluoro propyl, 2-(perfluoro-ethyl) ethyl, and 2-(perfluoro-butyl) ethyl, are mentioned.

[0020] As an example of R6, radicals, such as methylene, ethylene, a butylene, hexylene, a propylene, and decylene, the hydrocarbon group of the unsubstituted bivalence expressed with the following general formula (5), the hydrocarbon group of the bivalence which has a substituent like 2-hydroxypropyl, etc. are mentioned.

[Formula 8]

CH₃ CH₃ CH₃

|

| 又は

CH₃

(5)

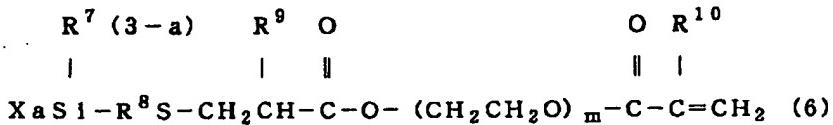
-CH₂CH₂CH- , -CH₂CH- -CH₂CHCH₂-

As an example of these sulphydryl group content silanes gamma-mercaptopropyltrimethoxysilane, gamma-mercaptopropyltriethoxysilane, Gamma-mercaptopropylmethyl dimethoxysilane, gamma-mercaptopropylethyl dimethoxysilane, gamma-mercaptopropylmethyl diethoxysilane, gamma-mercaptopropylethyl diethoxysilane, gamma-mercaptopropyl butyl dimethoxysilane, delta-mercaptopropyltrimethoxysilane, delta-mercaptopropyltriethoxysilane, delta-mercaptopropylmethyl dimethoxysilane, delta-mercaptopropylethyl dimethoxysilane, delta-mercaptopropylethyl diethoxysilane, delta-mercaptopropylethyl diethoxysilane, gamma-mercaptopropylethyl isobutyl trimethoxysilane, gamma-mercaptopropylethylmethyl dimethoxysilane, gamma-mercaptopropylethyltrimethoxysilane, gamma-mercaptopropylethylmethyl trimethoxysilane, gamma-mercaptopropyl-2-hydroxypropyl trimethoxysilane, gamma-mercaptopropyl-2-hydroxypropyltriethoxysilane, gamma-mercaptopropyl-2-hydroxypropylmethyl dimethoxysilane, gamma-mercaptopropyl-2-hydroxypropylethyl diethoxysilane, gamma-mercaptopropyl dimethyl METOKISHISHIRAN, gamma-mercaptopropyl diethyl ETOKISHISHIRAN, beta-mercaptopropylethyl trimethoxysilane, beta-mercaptopropylethyltriethoxysilane, gamma-mercaptopropyl triaminosilane, etc. are mentioned.

[0021] (Meta) The polyethylene GURIKORUJI (meta) acrylate as a raw material of an acrylic functionality silane compound has that desirable whose average molecular weight is 400 or less. When average molecular weight is too high, and it mixes with colloidal silica, the resin constituent for paint films with a good cause of condensation is not obtained.

[0022] As a Michael addition reaction object of a sulphydryl group content silane and polyethylene GURIKORUJI (meta) acrylate, what is expressed with a general formula (6) is desirable.

[Formula 9]

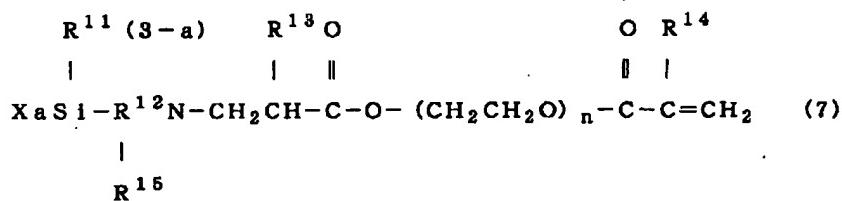


(As for the hydrocarbon group or fluorination alkyl group of monovalence, as for R7, a carbon number becomes independent, as for the permutation of the bivalence of 1-10 or an unsubstituted hydrocarbon group, and R9 and R10, R8 becomes independent, respectively, and a hydrogen atom or a methyl group is expressed.) In X, a hydrolysis nature machine and a express the integer of 1-3, and m expresses the integer of 1-9.

On the other hand, the amino-group content silane as a raw material of an acrylic (meta) functionality silane compound has N-(2-aminoethyl-3-aminopropyl) trimethoxysilane, 3-aminopropyl trimethoxysilane, desirable 3-aminopropyl triethoxysilane, etc.

[0023] As a Michael addition reaction object of an amino-group content silane and polyethylene GURIKORUJI (meta) acrylate, what is expressed with a general formula (7) is desirable.

[Formula 10]



(As for the hydrocarbon group or fluorination alkyl group of monovalence, as for R11, a carbon number becomes independent, as for the permutation of the bivalence of 1-10 or an unsubstituted hydrocarbon group, and R13 and R14, R12 becomes independent, respectively, and a hydrogen atom or a methyl group, and R15 express a hydrogen atom or the univalent hydrocarbon group of carbon numbers 1-10.) In X, a hydrolysis nature machine and a express the integer of 1-3, and n expresses the integer of 1-9.

Although they advance at a room temperature even if these Michael addition reactions do not have a catalyst, the reaction rate can be made to increase according to a catalyst. As a catalyst, a metal alkoxide, a piperidine, quarternary ammonium salt, a tertiary phosphine, etc. are mentioned. Especially, the height of catalytic activity and the ease of handling to a tertiary phosphine is desirable, and triphenyl phosphine is still more desirable. Moreover, a reaction rate can be made to increase further by carrying out in a solvent. A polar high thing like alcohol as a solvent is desirable. After reaction termination, when removing a solvent, the alcohol of low-boiling points, such as ethanol and isopropanol, is more desirable.

[0024] When the acrylic functionality silane compound expressed with a general formula (6) and a general formula (7) (meta) is compared, what is expressed with a general formula (6) is more desirable in respect of the balance of the distributed stability of the colloidal silica by which surface qualification was carried out, the fog resistance ability of the obtained paint film, a paint film degree of hardness, and film adhesion.

[0025] After applying to resin mold goods the resin constituent for paint films which generally uses a polyfunctional (meta) acrylate system monomer as a principal component, when hardening and forming a paint film, in order to acquire the adhesion to the resin mold goods by the so-called anchor effect, the approach of hardening, after making fixed time amount resin mold goods permeate is used [after applying the resin constituent for paint films] well.

[0026] In that case, when a polyfunctional (meta) acrylate system monomer is used as a principal component and the resin constituent for paint films permeates resin mold goods in the resin constituent for paint films with which colloidal silica was distributed, by the paint film after hardening, the gestalt with which colloidal silica was condensed by the paint film front face may be taken. In that case, when surface qualification of colloidal silica is performed by only the acrylic (meta) functionality silane compound, the crosslinking density on the front face of a paint film at the time of hardening increases very much, and may reduce fog resistance ability.

[0027] So, in the invention in this application, the hydrolyzate of an acrylic (meta) functionality silane compound and the hydrolyzate of a non-[hydrophilic] functionality silane compound are used together as a component which performs surface qualification of colloidal silica. Even when colloidal silica (d) is condensed by it on a paint film front face, the crosslinking density of a paint film cannot go up too much, and fog resistance ability can be maintained.

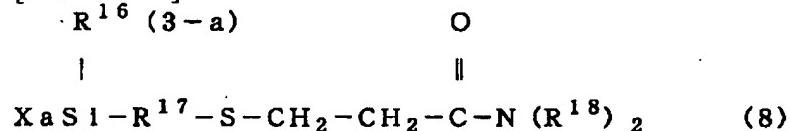
[0028] As for the hydrolyzate of this non-[hydrophilic] functionality silane compound, it is desirable to consist of hydrolyzate of the Michael addition reaction object of a sulphydryl group content silane or an amino-group content silane, and a hydrophilic monofunctional (meta) acrylic monomer.

[0029] The aforementioned thing is mentioned to the sulphydryl group content silane and amino-group content silane as a raw material of a non-[hydrophilic] functionality silane compound.

[0030] The hydrophilic monofunctional (meta) acrylic monomer as a raw material of a non-[hydrophilic] functionality silane compound N and N-dimethyl (meta) acrylamide, N, and N-dimethylaminooethyl (meta) acrylamide, Acrylamide (meta) system monomers, such as N and N-dimethylaminopropyl (meta) acrylamide and N-isopropyl (meta) acrylamide, 2-hydroxyethyl (meta) acrylate, 2-hydroxy butyl acrylate, acryloyl (meta) morpholine, polyethylene-glycol (meta) acrylate, alkyl phenoxy polyethylene-glycol (meta) acrylate, etc. are mentioned.

[0031] Especially since what is expressed with the general formula (8) which is the Michael addition reaction object of an acrylamide (meta) system monomer and a sulphydryl group content silane as a non-[hydrophilic] functionality silane compound can heighten the holding power to the inside of the adhesion of the paint film obtained, fog resistance ability, and the paint film of the added surfactant, it is desirable.

[Formula 11]



(R16 is the hydrocarbon group or fluorination alkyl group of monovalence, and, as for the permutation of the bivalence of 1-10 or an unsubstituted hydrocarbon group, and R18, in R17, a carbon number expresses the alkyl group of carbon numbers 1-5.) X expresses a hydrolysis nature machine and a expresses the integer of 1-3. HLB of the Nonion system surfactant which constitutes the resin constituent for paint films of this invention is the thing of 6-11. HLB is hydrophilic oleophilic balance here, and it is expressed with the following general formula (9) when molecular weight of Mw and a lipophilic group is set to Mo for the molecular weight of a hydrophilic group.

[Formula 12]

$$\text{HLB} = 7 + 1.1 \cdot 7 \times 10^g (M_w/M_o) \quad (9)$$

When HLB is lower than 6, the fog resistance ability of a paint film falls. When HLB is higher than 11, the adhesion of a paint film gets worse. The content of the Nonion system surfactant is 0.1 - 10 weight section to the polymerization nature monomer mixture 100 weight section, and its 1 - 7 weight section is more desirable. When the content of the Nonion system surface active agent is lower than the 0.1 weight section, it becomes difficult to balance fog resistance ability and a paint film degree of hardness. When the adhesion of a paint film falls when higher than 10 weight sections, or the mold goods with which the paint film was covered are left, the problem that the bleeding of a lot of Nonion system surface active agents is seen from a paint film front face arises. As for the Nonion system surfactant, what is expressed with a general formula (2) is desirable.

[0032] As an example of a surface active agent expressed with a general formula (2), the polyoxyethylene lauryl ether, the polyoxyethylene cetyl ether, polyoxyethylene stearylether, the polyoxyethylene oleyl ether, polyoxyethylene octyl phenyl ether, the polyoxyethylene nonylphenyl ether, etc. are mentioned.

[0033] As for the anion system surfactant which constitutes the resin constituent for paint films of this invention, what is expressed with a general formula (3) is desirable. This is obtained by perfect-neutralizing or partial

neutralizing the phosphoric-acid residue of the mixture of the phosphoric-acid diester independent of polyoxyethylene alkyl ether or phosphoric-acid monoester, and phosphoric-acid diester. Moreover, it is obtained by perfect-neutralizing or partial neutralizing the phosphoric-acid residue of the mixture of the phosphoric-acid diester independent of polyoxyethylene alkyl phenyl ether or phosphoric-acid monoester, and phosphoric-acid diester. As a concrete example of polyoxyethylene alkyl ether, the polyoxyethylene lauryl ether, the polyoxyethylene cetyl ether, polyoxyethylene stearylether, the polyoxyethylene oleyl ether, etc. are mentioned. Moreover, as a concrete example of polyoxyethylene alkyl phenyl ether, polyoxyethylene octyl phenyl ether, the polyoxyethylene nonylphenyl ether, etc. are mentioned. The content of an anion system surfactant is 0.1 - 5 weight section to the polymerization nature monomer mixture 100 weight section. When a content is lower than the 0.1 weight section, the fog resistance ability after the heat history gets worse. When higher than 5 weight sections, the non-melt of an anion system surfactant deposits in the resin constituent for paint films, or a lot of bubbles are generated by fizz increasing at the time of the churning dissolution, and the appearance of a paint film gets worse.

[0034] The polymerization initiator which constitutes the resin constituent for paint films can use the thing of arbitration. As a polymerization initiator, a benzophenone, a Michler's ketone, a benzoin, Benzoin ethyl ether, benzoin iso-propyl ether, benzoin isobutyl ether, Methyl benzoyl formate, 2-hydroxy - 2-methyl-1-phenyl propane-1-ON, ON 1-(4-isopropyl phenyl)-2- the id -- ROKISHI-isobutane-1- Benzyl dimethyl ketal, benzyl diethyl ketal, a diethoxy acetophenone, 1-hydroxy cyclohexyl phenyl ketone 2, a 2-dimethoxy-2-phenyl acetophenone, 2-methyl-[4-(methylthio) phenyl]-2-morpholino-1-propanone, An isopropyl thioxan ton, 2, 4-diethyl thioxan ton, 2 and 4, 6-trimethyl benzoyl diphenyl phosphine oxide, Thermal polymerization initiators, such as photopolymerization initiators, such as benzoyl diethoxy phosphine oxide, azobisisobutyronitril, azobis-2,4-dimethylvaleronitrile, benzoyl peroxide, and JITA challis butyl peroxide, etc. are mentioned. These polymerization initiators may be independent or may use two or more sorts together.

[0035] The content of a polymerization initiator is 0.01 - 10 weight section to the polymerization nature monomer mixture 100 weight section. When the content of a polymerization initiator is lower than the 0.01 weight section, the degree of hardness of the obtained paint film falls. When higher than 10 weight sections, paint film coloring and the fall of fog resistance ability occur.

[0036] As an approach of applying the resin constituent for paint films of this invention to a resin mold-goods front face, the roll coater method, the knife coating-machine method, a dip coating method, a spray coating method, etc. are mentioned. Moreover, in order to obtain the resin mold goods with which the paint film which has good fog resistance ability was covered, as for the thickness of the paint film by which polymerization hardening was carried out, it is desirable that it is 5-100 micrometers. Therefore, it is desirable to choose the method of application which can obtain desired thickness according to the viscosity of the resin constituent for paint films. Manufacturing a resin plate, the resin constituent for paint films is applied to a resin plate, polymerization hardening can be carried out, and the resin plate with which the paint film was covered continuously can also be obtained.

[0037] Although thermal polymerization, a photopolymerization method, etc. can be used as an approach of carrying out polymerization hardening of the resin constituent for paint films, it is desirable to use a photopolymerization method in respect of energy cost etc. Moreover, at the time of a polymerization, in order to avoid the polymerization inhibition by oxygen, it is desirable to carry out polymerization hardening under inert gas ambient atmospheres, such as nitrogen. It is also desirable to carry out polymerization hardening under the ambient atmosphere which covered the resin constituent for paint films with a resin film or mold, and intercepted air.

[0038] Moreover, an ultraviolet ray absorbent, light stabilizer, a thermostabilizer, a solvent, a thickener, an inorganic filler, etc. can be added in the resin constituent for paint films if needed.

[0039] As resin mold goods with which the paint film which consists of a hardened material of the resin constituent for paint films of this invention is covered, mold goods, such as acrylic resin, polycarbonate resin, polystyrene resin, and polyester resin, are mentioned. The mold goods of acrylic resin and polycarbonate resin are desirable in respect of the transparency of resin, and the adhesion of a paint film. The resin mold goods with which the paint film which consists of a hardened material of the resin constituent for paint films of this invention was covered are excellent in abrasion-proof nature, endurance, and fog resistance, and suitable for skiing goggles, a helmet shield, meter covering, a spectacle lens, a face plate, etc.

[0040]

[Example] Hereafter, an example explains this invention. In addition, this invention is not limited to the following

examples. In each example, it is components added superfluously [in case the front face of colloidal silica is embellished], such as polyethylene GURIKORUJI (meta) acrylate and a hydrophilic monomer, and the unreacted component was indicated to Table 1 as a component which constitutes polymerization nature monomer mixture. In addition, the following conditions estimated each physical properties of the resin mold goods (suitably henceforth a "sample") with which the paint film was covered.

[0041] (1) Exhalation was blown upon the paint film side for the evaluation sample by fog resistance (1-1) exhalation from the distance of 20-30mm under this environment after 24-hour air conditioning under the environment of 50RH% at 23 degrees C, and the cloudy generating condition was observed and evaluated. O blowing exhalation every 10 times during 2 seconds for **[which has neither cloudy generating nor the fall of fluoroscopy nature even if it blows exhalation every 10 times during :2 seconds]:2 seconds, although there is no cloudy generating even if it blows exhalation While [x:2 seconds] fluoroscopy nature fell, the sample was installed so that a paint film might be on the environment side of 95RH% at 40 degrees C by 40 degrees C with the environment of 60RH% on a boundary with the environment of 95RH% by endurance (1-2) evaluation of 23 degrees C which cloudiness generates by blowing exhalation, change of fluoroscopy nature was observed for 1 hour, and viewing estimated it.

O : -- generating of x:cloudiness which cloudiness was not generated, but the whole paint film surface got wet equally, and the condition with good fluoroscopy nature continued for 1 hour or a paint film is uneven -- getting wet -- after making the 100 1mmx1mm squares from the cutter to the paint film of the adhesion sample of (2) paint films to which fluoroscopy nature fell and sticking adhesive tape (Nichiban Co., Ltd. make) on this, the number of the squares which repeated tearing off adhesive tape rapidly 3 times, and did not exfoliate it was counted, and adhesion was evaluated.

[0042] (3) Abrasion-proof nature (delta haze)

Having placed the circular pad with a diameter [equipped with the steel wool of 000] of 25.4mm on the paint film side front face of a sample, and applying 1000g of loads, the both-way abrasion of the distance of 20mm was carried out 100 times, and it asked by the following formula by making the difference of the haze value an abrasion front and after an abrasion into ** haze.

The haze value in front of the haze value (%) - abrasion after a delta haze (%) = abrasion (%)

(4) After leaving a sample for five days under the environment of 60 degrees C of moisture resistance, and 95RH%, the paint film at the time of grinding a paint film against a pawl got damaged, and the sex was evaluated.

O : -- **: which does not get damaged at all -- single curved-surface bending shaping was performed so that a paint film side might be [at the hot-air-drying furnace containing a blemish which x: is 165 degrees C of (5) thermoforming nature from which a paint film falls out when it grinds] on a concave surface side after heating using a pattern with a radius of curvature of 40mm for 10 minutes about a sample, and the generating situation of a crack was observed.

[0043] Reacted the 100 weight sections and the 3-% of the weight isopropanol solution of triphenylphosphine by 45 weight sections sequential *****, the solution was made for KBM-803 (Shin-Etsu Chemical Co., Ltd. make) which is the 100 weight sections and gamma-mercapto propyltrimethoxysilane about the 156 weight sections and dimethyl acrylamide (henceforth "DMAA") in isopropanol to react to the [example 1] flask A for three days at a room temperature, and the non-[hydrophilic] functionality silane compound was compounded.

[0044] Subsequently, added 70 weight sections for the NK ester A-200 (it is called "A-200" the product made from New Nakamura Chemistry, and the following) which is 71 weight sections and polyethylene-glycol diacrylate of molecular weight 200 about isopropanol to Flask B, added 14 weight sections and the 3-% of the weight isopropanol solution 9.1 weight section of triphenylphosphine for KBM-803 one by one, the solution was made to react to 60 degrees C after a temperature up for 3 hours, and the acrylic functionality silane compound was compounded.

[0045] It 234-weight-***** (ed), IPA-ST (Nissan Chemical Industries, Ltd. make) which is colloidal silica of 30 % of the weight of solid content which makes isopropanol a dispersion medium was ranked second to the obtained reaction mixture, the hydrochloric-acid water-solution 6 weight section of the centinormal was added, it stirred at 60 degrees C for 1 hour, and the front face of colloidal silica was embellished with the hydrolyzate of an acrylic functionality silane compound.

[0046] The mixture 56 weight section containing the non-[hydrophilic] functionality silane compound in Flask A

and the hydrochloric-acid water solution of the centinormal were made to react to Flask B at 6 weight ***** and 60 more degrees C for 1 hour, and the front face of colloidal silica was embellished.

[0047] Subsequently, LO-529 (Toho Chemical Industry Co., Ltd. make) which is the emulgen 905(Kao Corp. make) 7 weight section and anion system surfactant phosphor Norian of a general formula (3) 53 weight sections and whose HLB are the Nonion system surfactants of 9.2 about the NK ester A-400 (it is called "A-400" the product made from New Nakamura Chemistry and the following) which is polyethylene-glycol diacrylate of molecular weight 400 was distilled off by 4.2 weight ***** to this reaction mixture, and that mixture was distilled off under reduced pressure of a volatile component in the rotary evaporator.

[0048] Lucirin which is 2, 4, and 6-trimethyl diphenyl phosphine oxide at this reaction mixture 100 weight section considering 1,6-hexanediol diacrylate (it is called "C6DA" the OSAKA ORGANIC CHEMICAL INDUSTRY, LTD. make and the following) as 5 weight sections and a polymerization initiator The 1.5 weight ***** dissolution of the TPO (it is called "TPO" the BASF A.G. make and the following) was carried out, and the resin constituent for paint films was manufactured.

[0049] The resin constituent for paint films was applied on the polycarbonate plate (it is called a "PC board" the diamond light by Mitsubishi Rayon Co., Ltd., and the following) with a thickness of 2mm which carried out preheating at the 60-degree C hot-air-drying furnace. Furthermore, the biaxial oriented film with a thickness of 50micro made from polyethylene terephthalate (it is called a "PET film" the Teijin, Ltd. make and the following) was put on it, and thickness of cover printing and the resin constituent for paint films was set to 12micro with the rubber covered roll with a JIS degree of hardness of 40 degrees. After leaving it for 50 seconds after that, a PET film plane is made into a lamp side for the place distant from the ozone loess type metal halide lamp of output 120 w/cm 210mm, the PC board was passed at the speed of 1.6 m/min, and polymerization hardening is carried out. The PET film was exfoliated after that and the PC board with which a paint film side is made into a lamp side for the place which is further distant from the ozone loess type high-pressure mercury lamp of output 120 w/cm 210mm, the PC board was passed at the speed of 1.6 m/min, polymerization hardening was completed, and the paint film was covered was obtained. In addition, after setting the thickness of the resin constituent for paint films as 12micro, the temperature before the exposure of a metal halide lamp and on a PET film front face was 40-43 degrees C.

[0050] The evaluation result of the PC board with which the obtained paint film was covered is shown in Table 1.

[0051] Except having made the amount of [example 2] C6DA into 10 weight sections, the resin constituent for paint films was manufactured like the example 1, and the paint film was covered to the PC board. An evaluation result is shown in Table 1.

[0052] Instead of the [example 3] DMAA100 weight section, except having used the acryloyl morpholine (henceforth "ACMO") 100 weight section, the resin constituent for paint films was manufactured like the example 1, and the paint film was covered to the PC board. An evaluation result is shown in Table 1.

[0053] Except having not added [example 1 of comparison] C6DA, the resin constituent for paint films was manufactured like the example 1, and the paint film was covered to the PC board. An evaluation result is shown in Table 1.

[0054] Except having made the amount of [example 2 of comparison] C6DA into 25 weight sections, the resin constituent for paint films was manufactured like the example 1, and the paint film was covered to the PC board. An evaluation result is shown in Table 1.

[0055] The front face of colloidal silica was embellished with the hydrolyzate of an acrylic functionality silane compound like the [example 3 of comparison] example 1.

[0056] subsequently, this reaction mixture -- A-200 -- 68 weight sections and emulgen 905 were distilled off in 7 weight sections, and 4.2 weight ***** mixture was distilled [12 weight sections and A-400] off for phosphor Norian LO-529 under reduced pressure of a volatile component in the rotary evaporator.

[0057] In this reaction mixture 100 weight section, the 1.5 weight ***** dissolution of 5 weight sections and the TPO was carried out for C6DA, the resin constituent for paint films was manufactured, and the paint film was covered to the polycarbonate plate in it. An evaluation result is shown in Table 1.

[0058] The IPA-ST200 weight section was added to the [example 4 of comparison] flask, 12 weight sections and the hydrochloric-acid water-solution 4.5 weight section of the centinormal were added, KBM-103 (Shin-Etsu Chemical Co., Ltd. make) which is subsequently phenyl trimethoxysilane was stirred at 60 degrees C for 1 hour, and the front face of colloidal silica was embellished with the hydrolyzate of a non-hydrophilic-property non-

functionality silane compound.

[0059] subsequently, this reaction mixture -- A-200 -- the 31.2 weight sections and emulgen 905 were distilled off in the 4.5 weight sections, and 2.7 weight ***** mixture was distilled [the 46.8 weight sections and A-400] off for phosphor Norian LO-529 under reduced pressure of a volatile component in the rotary evaporator.

[0060] In this reaction mixture 104.8 weight section, the 1.5 weight ***** dissolution of the TPO was carried out, the resin constituent for paint films was manufactured, and the paint film was covered to the polycarbonate plate in it. An evaluation result is shown in Table 1.

[0061] KBM-503 (Shin-Etsu Chemical Co., Ltd. make) which is gamma-methacryloxypropyl trimethoxy silane instead of [example 5 of comparison] KBM-103 was used, except having embellished the front face of colloidal silica with the hydrolyzate of an acrylic functionality silane compound, the resin constituent for paint films was manufactured like the example 4 of a comparison, and the paint film was covered to the polycarbonate plate. An evaluation result is shown in Table 1.

[0062] The non-[hydrophilic] functionality silane compound was compounded like the [example 6 of comparison] example 1.

[0063] Subsequently, the mixture 56 weight section which contains a non-[hydrophilic] functionality silane compound for IPA-ST with the 234 weight sections, and the hydrochloric-acid water-solution 6 weight section of the centinormal were added. Colloidal silica was not able to condense by addition of a non-[hydrophilic] functionality silane compound, it was not able to become gel, and the resin constituent for paint films was not able to be manufactured.

[0064]

[Table 1]

		実施例1	実施例2	実施例3	比較例1	比較例2	比較例3	比較例4	比較例5
塗膜用樹脂組成物	(a) A-200 A-400	19.4 21.5	18.5 20.4	19.4 21.4	20.4 22.5	16.2 17.9	24.3 27.6	31.2 20.8	31.2 20.8
	(b) C6DA	5.0	9.4	5.0	-	20.8	5.0	-	-
	(c) DMAA ACMO	3.8 -	3.6 -	- 1.6	4.0 -	3.1 -	- -	- -	- -
	(d) 表面が修飾されたコロイドシリカ	50.4	48.1	52.6	53.1	42.1	43.1	48.0	48.0
	ノニオン系界面活性剤 E-905	2.8	2.7	2.8	3.0	2.4	2.8	3.0	3.0
	アニオン系界面活性剤 LO-529	1.7	1.6	1.7	1.8	1.4	1.7	1.8	1.8
	重合開始剤TPO	1.5	1.4	1.5	1.6	1.2	1.5	1.5	1.5
物理評価	防霧性: 呼気による評価 耐久性評価	○ ○	○ ○	○ ○	○ ○	△ ×	○ ×	○ ×	△ ×
	塗膜の密着性	100/100	100/100	100/100	100/100	100/100	100/100	98/100	100/100
	耐擦傷性(△ヘーツ)	2.1	1.8	2.0	2.5	1.1	1.2	1.6.0	1.1
	耐熱性	○	○	○	×	○	○	-	-
	熱成形性	良好	クラック発生						

[0065]

[Effect of the Invention] According to this invention, it excels in fog resistance ability, thermoforming nature, the adhesion of a paint film, and abrasion-proof nature, and the resin mold goods with which the outstanding paint film which neither the fall of the fog resistance ability by thermoforming nor the degree-of-hardness fall at the time of water absorption also has was covered can be obtained. Moreover, the hardened material of the resin constituent for paint films of this invention fits the above-mentioned paint film.

[Translation done.]

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